A Multi-scale Computational Approach for Nanoparticle Growth in Combustion Environments

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Abstract. In this paper a new and powerful computer simulation capability for the characterization of carbonaceous nanoparticle assemblies across multiple, connected scales, starting from the molecular scale is presented. The goal is to provide a computational infrastructure that can reveal through multi-scale computer simulation how chemistry can influence the structure and function of carbonaceous assemblies at significantly larger length and time scales. Atomistic simulation methodologies, such as Molecular Dynamics and Kinetic Monte Carlo, are used to describe the particle growth and the different spatial and temporal scales are connected in a multi-scale fashion so that key information is passed upward in scale. The modeling of the multiple scales are allowed to be dynamically coupled within a single computer simulation using the latest generation MPI protocol within a grid-based computing scheme.

1 Introduction

A detailed description of high molecular mass particle formation in combustion systems, such as a flame environment, can be viewed as comprised of two principal components: gas-phase chemistry and particle dynamics, which describes the evolution of the particle ensemble. Figure 1 [1] summarizes the different pathways describing the formation of nanoparticle agglomerates starting from simple fuels, going through the formation of polycyclic aromatic hydrocarbons (PAH) [2-8], particle inception, particle coagulation leading to primary particles (50 nm in diameter) [9-17], ending up with their particle agglomerates (~500 nm in diameter).

As reported in fig. 1, the processes involved in the particle formation exhibit a wide range of time scales, spanning pico- or nanoseconds for intramolecular processes to milliseconds for intermolecular reactions. At the same time, the length scale also undergoes significant changes going from a few angstroms for small PAH to hundreds of nanometers for particle aggregates.

The goal of this work is the development of multi-scale atomistic approaches to study the formation and fate of carbonaceous material, in a chemically specific way. The reason for seeking the structural information of the particles is due to the importance that particles emitted from combustion sources have in the environment. Two main problems are related to the presence of aerosols in the atmosphere: the health impact and the climate change. Once the chemical structures of these particles are known, challenging problems, such as their interaction with biological systems and the optical properties relevant to direct radiative forcing, can be addressed.

L.T. Yang et al. (Eds.): HPCC 2005, LNCS 3726, pp. 938 – 947, 2005.

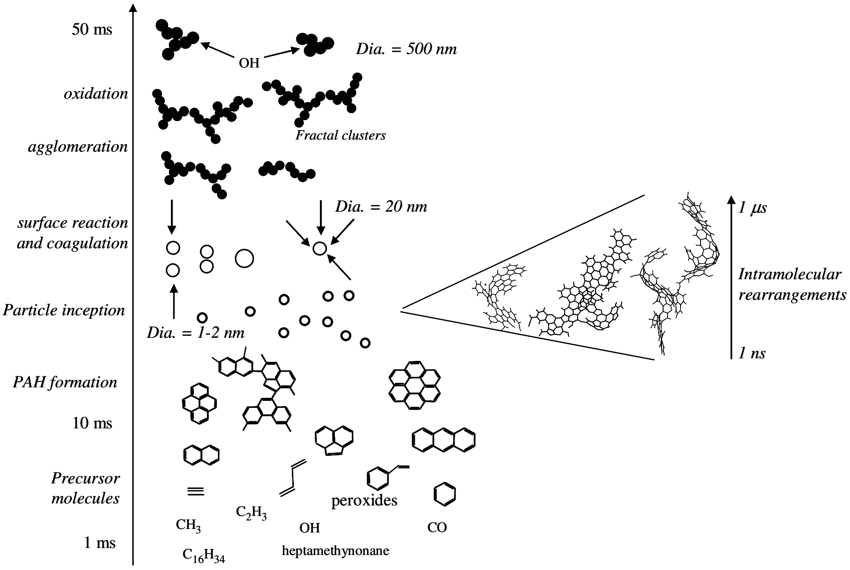

Fig. 1. Processes involved in the formation of particles in flames

There is no attempt in the literature to study the processes involved in the formation of particles using an atomistic representation, and this paper reports on the work we pioneered for nanoparticle growth in combustion.

In the following sections, it will be shown how a new multi-scale simulation can be created and applied to the formation of carbon nanoparticles. The methodology will allow us to follow the transformations that occur during nanoparticle formation in a chemically specific way, providing information on both the chemical structure and the configuration of the nanoparticles and their agglomeration.

The primary goal of this work is to provide the computational infrastructure to help connect molecular properties with the behavior of particle systems at much larger length and time scales. This new computational approach can reveal the role of chemical changes at the molecular level in defining the functional behavior of nanoparticle assembly. In particular, this approach will help us to understand how specific chemical structures or changes at the scale of the molecular building blocks will influence the emergent structure and function of particle assembly at larger length and time scales.

This effort will involve the development of underlying modeling concepts at the relevant scales, the multi-scale linking of these scales, and finally the computational execution of the multi-scale simulations using a novel MPI grid computing strategy.

2 Methodology

Keeping in mind that the overarching goal of this work is the development of a computational paradigm capable of coupling chemical scales to much longer length-scale assembly processes, the multi-scaling thus begins at an atomistic-level of

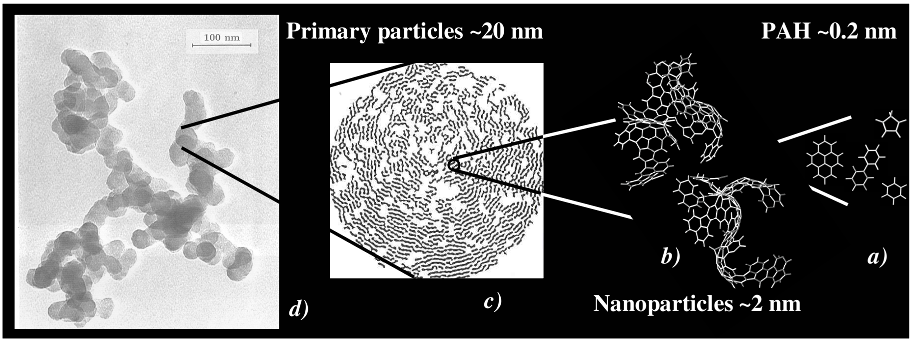

Fig. 2. Computational multi-scale coupling scheme for particle formation

resolution where gas-phase PAH monomers (*a* in Fig. 2) are used to build a larger system of nanoparticles having a diameter of 2-3 nm (*b*), which in turn represent the monomers for the following growth into primary particles with an average diameter of ~20 nm (*c*) and eventually particle agglomerates of ~500 nm (*d* in Fig. 2).

After a description of the methodologies used to go from simple gas-phase PAH monomers to the formation of nanoparticles (*a-b*) and then to particle agglomeration (*c-d*), section 2.3 will report on the computational modeling infrastructure that allows the atomistic methods to be dynamically coupled within a single computer simulation using the latest generation MPI protocol within a grid-based computing scheme.

It is important to keep in mind that although presented in separate sections, the phenomena of nanoparticle formation and their further agglomeration and growth into bigger units occur simultaneously. In other words, once nanoparticles are formed and start to agglomerate, PAH monomers from the gas phase can still contribute to the growth through surface reactions and the information is produced at the lower scale needs to be carried out to the largest scale.

2.1 From Gas-Phase Monomers to Nanoparticle Inception

The simulation methods for many-body systems can be divided into two classes of stochastic and deterministic simulations, which are largely covered by Monte Carlo method and Molecular Dynamics method, respectively. Kinetic Monte Carlo (KMC) simulations [18-19] solve the evolution of an ensemble of particles in configuration space, provided some initial condition, and a complete set of transition events (chemical reactions, diffusion events, etc.). By contrast Molecular Dynamics (MD) solves the trajectories of a collection of atoms in phase space (configuration + momentum) given the initial conditions and potential. This is an advantage of MD simulation with respect to KMC since not only is the configuration space probed but also the whole phase space, which can give more information about the dynamics of the system, subject to any additional constraints on the equations of motion. However, the limitation in the accessible simulation time represents a substantial obstacle in making useful predictions with MD. Resolving individual atomic vibrations requires a time step of approximately femtoseconds in the integration of the equations of motion, so that reaching times of microseconds is very difficult.

With the aim of keeping an atomistic description of the system and at the same time to be able to cover large time scales, such as milliseconds for the particle inception (see time scale in Figure 1), the MD and KMC methodologies have been coupled to extend the accessible time scale by orders of magnitude relative to direct MD, (Atomistic Model for particle Inception Code – AMPI) [20-21]. The time-step for a single KMC iteration is a ‘‘real time,’’ determined by the kinetics system.

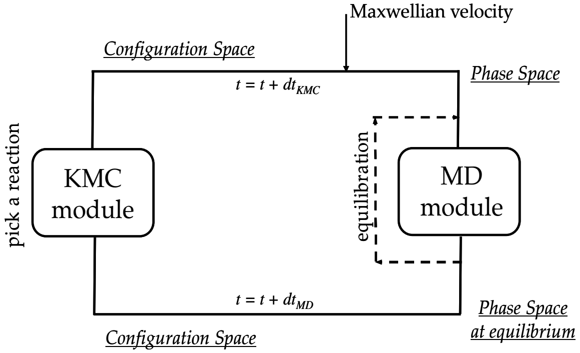

Fig. 3. Schematic of the AMPI code

The reaction rates among the compounds present in the system are specified as probabilities, and the surface configuration over time is then given by a master equation, describing the time evolution of the probability distribution of system configurations. The AMPI code couples the two techniques in a novel way, placing both of them on equal footing with a constant alternation between the two modules. Figure 3 shows a schematic representation of the AMPI code. Since theoutput of the KMC module is a configuration space, while the input to the MD part is represented by the phase space (configuration + momentum), velocities are assigned to the atoms of the growing seed according to a Maxwell–Boltzmann distribution function after exiting the KMC module. The KMC and MD methods therefore, differ in their effective ability to explore conformation space.

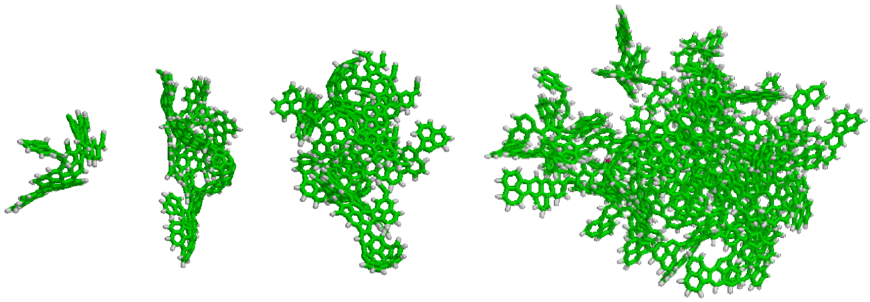

Fig 4. Carbonaceous nanoparticles

In a typical simulation, an aromatic seed molecule is placed in a reacting environment described by 1) temperature, 2) number and concentrations of the monomers in the gas-phase that can contribute to the growth process and 3) reaction rates between the monomers and the seed. The code alternates between the KMC and MD modules: during a KMC time step one reaction is executed at one site on the growing aromatic structure. The probability of choosing a particular reaction is equal to the rate at which the reaction occurs relative to the sum of the rates of all of the possible reactions for the current configuration. For each time step, one reaction is chosen from the probability-weighted list of all of the events that can possibly occur at that step. The molecular system is then altered, and the list of relative rates is updated to reflect the new configuration. The MD module, run after each KMC step, allows for relaxation of the molecules towards thermal equilibrium. Figure 4 shows the structures of carbonaceous nanoparticles produced with the AMPI code. For the specific example reported in Fig. 4 acetylene, naphthalene, acenaphthylene and their radicals, respectively are used as gas-phase monomers that can contribute to the growth of an initial seed represented by naphthalene in a specific environment of benzene-oxygen laminar premixed flame.

2.2 From Nanoparticle Inception to Agglomerates

As soon as the first nanoparticles are formed, they start reacting with each other. Carbonaceous nanoparticle agglomeration is influenced by large length and time scale motions that extend to mesoscopic scales, i.e., one micrometer or more in length and one microsecond or more in time. At the same time, the effects of various important intra-nanocluster processes, such as fragmentation, slow conformational rearrangements, ring closure and associated reactions need to be addressed to produce a realistic description of the particle growth phenomenon.

In order to increase the time and length scales accessible in simulations to be able to simulate nanoparticle assembly, a different methodology, via accelerated dynamics is proposed.

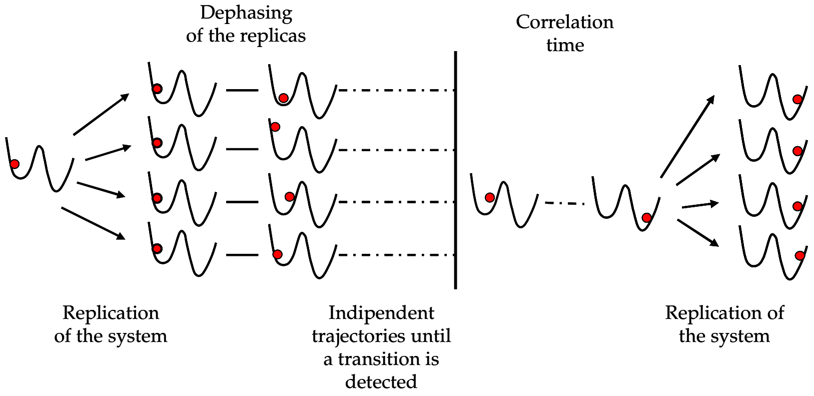

Fig. 5. Schematic of the PR MD architecture [23]

Given a resource of M processors in a parallel architecture, we employed a temporal parallelism to simulate different sections of the long-time dynamics on each of the M processors, rather than attempting to simulate each timestep M times faster. Among accelerated dynamic methods, the PRMD [22-23-24] is the simplest and most accurate method and it dramatically extends the effective time scale of an MD simulation. In the PR method, starting with an N atom system in a particular state, the system is replicated on many processors. After a dephasing stage, where momenta

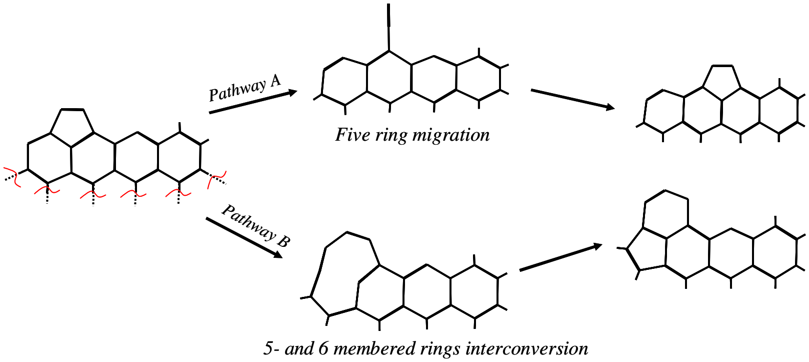

Fig. 6. Surface rearrangement reactions

are randomized, each processor carries out an independent MD trajectory. Each replica trajectory is monitored for a transition event by performing a quench after each $\Delta T_{\mathrm{block}}$ of integration time. When one processor (i) detects an event, all processors are notified to stop. The simulation clock is incremented by the sum of the trajectory times accumulated by all M replicas since the beginning, and the PR simulation is restarted, continuing onward until the next transition occurs and the process is repeated. Figure 5 reports a schematic for the Parallel Replica architecture [24]. Within the PR method, the effective time of the MD simulation is “boosted” significantly: the overall rate of some event is thus enhanced by a factor of M so that the probability of observing an event for the first time at a simulation time in the interval (t_l, t_l+dt_l) changes from $p(t_l)dt_l = ke^{-kt_l}dt_l$ for a single-processor simulation to $p(t_l)dt_l = Mke^{-kt_l}dt_l$ when simulating on M processors.

The use of PR MD for an enseble of nanoparticles produced with the AMPI code allows the identification of intramolecular as well as intermolecular reactions [1-2]. As an example, Fig. 6 shows possible rearrangement reactions that can occur on the particle surface. The particle considered has 289 C atoms but in Fig. 6, for clarity, only the region where the modification occurs is reported. Two mechanisms are highlighted: in pathway A the transformation is initiated by β-scission followed by the formation of a five membered ring similar to the initial one but shifted by one aromatic ring. The second pathway involves the transposition of 5- and 6-membered rings.

4 Multi-scale Coupling and Computational Grid Implementation

As stated before, nanoparticle inception from gas-phase species and particle agglomeration processes occur simultaneously and reconstituting the system in different spatial and temporal domains without bridging and linking the different scales, results in a sequence of independent spatial/temporal representations of the system. Without some means of coupling the scales each new representation of the overall multi-scale simulation methodology remains isolated from the other constituents. This limitation can restrict the ability of the multi-scale simulation methodology in directly complementing experimental work, as most of the experimental combustion spans a wide range of length and time-scales. For the formation of nanoparticles, the chemistry that occurs at the lower scale modifies the properties of particles and dictates the clustering behavior. The example reported in Fig. 6 for the particle surface can clarify this concept. The five membered ring is formed through the addition of acetylene from the gas-phase to the aromatic particle surface and the five-member-ring migration has important implications to surface growth of particles. For example, a "collision" of these propagating fronts may create a site that cannot be filled by cyclization and thus cannot support further growth. Formation of such surface defects may be responsible for the loss of reactivity of soot particle surface to growth. In essence, the newly nucleated particles grow by coagulation and coalescent collisions as well as surface growth from gas-phase species and the changes that can occur on single nanoparticles due to surface growth needs to propagate upward to the PR module.

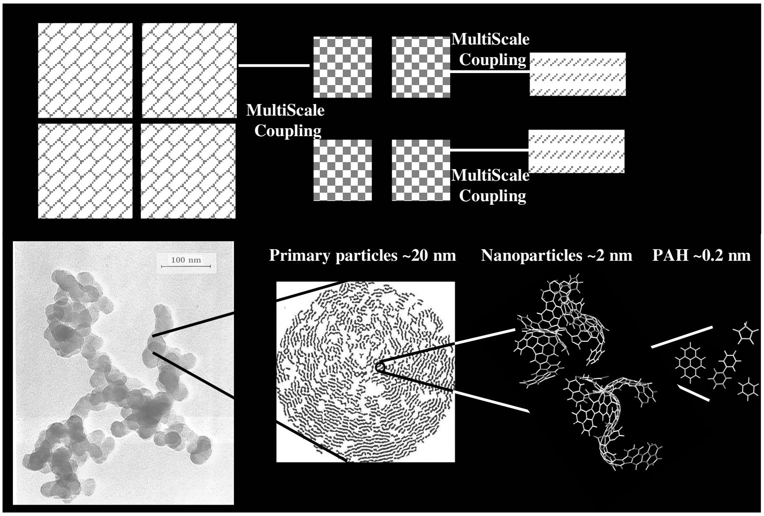

Fig. 7. Different grid schemes for each parallelization level

Each different process of the nanoparticle formation is modeled with a separate simulation suite. The parallel decomposition of the full multi-scale methodology is a critical component of the infrastructure. Each of the platforms (AMPI code and PR MD) has its own internal degree of parallelization. The novel infrastructure parallelization component consists in a new level of intra-parallelism: the aim is to construct a dynamic communication interface between the various simulation components of the multi-scale methodology, such that different codes can essentially speak to each other on the fly. The novelty of this approach is that a new level of communication is established between different programs with each program running on a separate computational platform. When combined with the intrinsic internal process communication, the result is a dual parallel communication scheme characterized by infrequent communication and the more familiar frequent large communication. Thanks to relatively recent adoption of the MPI-2 standard in major

MPI implementations, it is now feasible to implement communication schemes between separate programs. In particular, new programs (slave processes – PR MD in this case) can be launched via MPI-2 from an already running application (the master process – AMPI code) via an MPI-2 dynamic process creation. A series of interconnected communication channels can be established between the separate programs resulting in a communication interface that can be used to couple the slave and master processes, see Fig. 7. In other words, a set of distinct simulation methodologies, can be fused into one unified computational platform. The degree of fusion can be tuned to the specific problem. This extension leads to the opportunity of creating multi-level parallel applications where each of the sub-levels also operates under its own internal parallelization sub-grid. Both the fast internal parallelization as well as the mew multi-scale inter-process communication can be incorporated with each code using the MPI-2 standard. Figure 8 shows two examples of particle agglomeration obtained through the use of this new multi-scale infrastructure. The figure shows two snapshots from the multi-scale simulations of a system composed of 27 identical round particles (left panel) and a system of 27 flat particles produced in aliphatic flames (right panel). The simulations were performed at 1600K. The round particles tend to cluster and they show a preferred orientation that is back to back. The sheet-like particles show a different behavior: some of them drift away from the ensemble, some do cluster in small agglomerates. Therefore, the agglomeration behavior of nanoparticles is influenced by their morphology. This is an example of the kind of information necessary to build a realistic model for particle formation (for this example 164 Opteron nodes, 328 processors, 2 Gbytes memory per node were used).

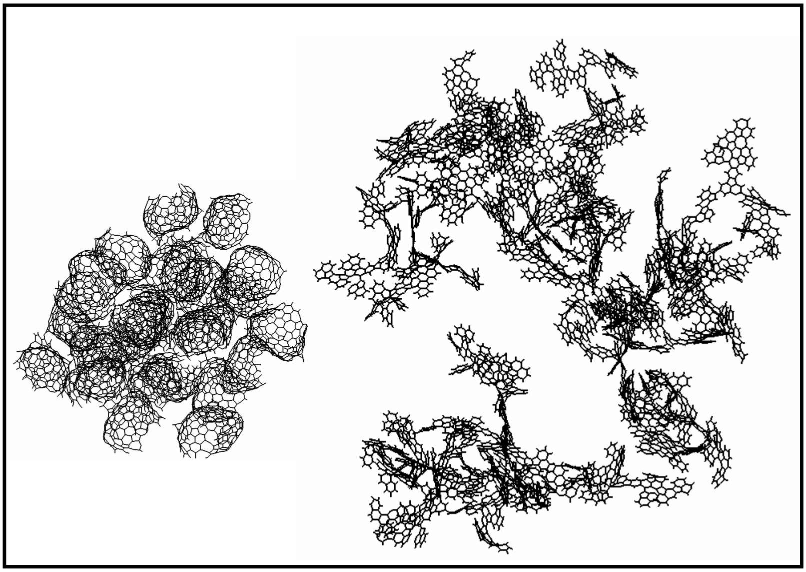

Fig. 8. Particle agglomerates

6 Conclusions

A new multi-scale computer simulation and modeling capability is presented to study the formation of carbonaceous nanoparticles in combustion systems. This methodology provides a framework that can better mimic the chemical and physical processes leading to nanoparticle soot particle inception and growth. The systematic multi-scaling begins at an atomistic-level of resolution where atomistic molecular dynamics simulations are employed to give quantitative predictions for the formation of the first nanoparticles and provide a computational template in which to base the next steps of the overall multi-scale computational paradigm.

This approach provides a connection between the various time scales in the nanoparticle self-assembly problem, together with an unprecedented opportunity for the understanding of the atomistic interactions underlying carbonaceous nanoparticle structures and growth. The scales are dynamically linked with each other and the execution of the full multi-scale simulation involves the use of a novel MPI and grid computing strategy.

Acknowledgments

This research is funded by the University of Utah Center for the Simulation of Accidental Fires and Explosions (C-SAFE), funded by the Department of Energy, Lawrence Livermore National Laboratory, under subcontract B341493 and by a National Science Foundation Nanoscale Interdisciplinary Research Team grant (EEC-0304433). The calculations presented in this paper were carried out at the Utah Center for High Performance Computing (CHPC), University of Utah that is acknowledged for computer time support. The authors thank Dr. A. Voter for providing us with the PRMD code.

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