Soot primary particle formation from multiscale coarse-grained molecular dynamics simulation

Angela Violi [*], Sergei Izvekov [1]

*Department of Mechanical Engineering, The University of Michigan, 2150 G.G. Brown,
2350 Hayward Street, Ann Arbor, MI 48109-2125, USA*

Abstract

A new multiscale coarse-graining procedure is used to study carbonaceous nanoparticle agglomeration in combustion environments. The computational methodology is applied to an ensemble of 10,000 nanoparticles (or effectively 2 million total carbon atoms) to simulate, for the first time, the agglomeration of carbonaceous nanoparticles using coarse-grained atomistic-scale information. In particular, with the coarse-graining approach we are able to assess the influence of nanoparticle morphology and temperature on the agglomeration process. The coarse-graining of the interparticle force field is accomplished applying a force-matching procedure to data obtained from trajectories and forces from all-atom MD simulations. The coarse-grained MD results show rich and varied clustering behaviors for different particle morphology and, in some cases, the formation of primary particles with a diameter around 15 nm are observed for the first time by molecular simulation techniques.
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1. Introduction

Soot formation in fuel-rich combustion represents the most studied case of nanoparticle formation in high temperature and highly reacting flows. Particle growth in the range 1–10 nm represents the most significant mass gain of the primary spherical particles ($\sim$50 nm in diameter) that further coalescence into aggregates. The rate of the nanoparticle growth not only determines the final soot mass, it also influences other soot properties such as morphology and composition. The capability to follow the nucleation and growth of nanoparticles in flames is crucial to arrive at a quantitative understanding of soot formation in flames.

There have been several principal hypotheses made regarding the general nature of soot particle inception including processes involving polyacetylenes [1], ionic species [2], or PAH [3] as the key gaseous precursors to soot [4–9].

The essence of the models present in the literature is the increase in particle mass by chemical reactions with gaseous precursors simultaneously with the growth of particle size by collision among PAH molecular species and clusters. Most simulations are carried out up to a specified aromatic size, e.g., 4 rings, while some treat the aromatic growth without limit using a linear lumping technique [10]. The transition from the gas phase to

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[*] Corresponding author. Fax: +1 734 647 9379.
E-mail address: avioli@umich.edu (A. Violi).
[1] Permanent address: Department of Chemistry, University of Utah, Salt Lake City, UT 84112, USA.

particles is handled by assuming the nucleation to take place at the collision of pyrene and larger aromatics [11–19] or at the collision of benzene molecules [20,21]. The accumulation of particle mass via chemical reactions with gaseous precursors simultaneously with the growth of particle size by collision among PAH molecular species and clusters was used to describe the particle growth process. Surface growth was treated either empirically or based on chemical analogy to aromatics chemistry. The coagulation of soot particles was modeled using either a discrete-sectional method [16,22] or the method of moments [20,23].

The large size of these models needed to describe the high molecular weight species can be reduced by applying various mathematical methods that reduce the size of the mathematical formulation. For example, in the discrete sectional methods [24], the entire particle ensemble is divided into several dozens of sections and the particle properties are averaged within each section. These methods can be used to yield information about soot particle distribution, but are limited by the number of sections that can be treated with acceptable computing times. In the methods of the moments [25] the description of particle dynamics is reformulated in terms of moments of the particle size distribution function.

These methods offer mathematical simplicity but do not yield chemical detail on the higher molecular weight species. To help resolve issues such as identification of pathways leading to soot formation, it is important to characterize the precursors, in terms of chemical structure/components. 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 this paper, we report on an innovative multi-scale characterization of nanoparticle formation in combustion environments, through the use of novel coarse-grained molecular simulation methodologies at disparate (spatial/temporal) regimes. Predictive models of nanoparticle formation and oxidation that provide detailed chemical structures of the particles currently do not exist, a fact that greatly limits our ability to control this important chemical process. The use of atomistic models, such as kinetic Monte Carlo technique and Molecular Dynamics, can 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. This approach provides a connection between the various time and length 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 objective of this paper is to report on the new multiscale coarse-graining method to study carbonaceous nanoparticle growth into primary particles and identify the role of morphology and temperature on the agglomeration process. After describing in the next section the computational methodologies employed, a detailed discussion of the rich and interesting nanoparticle agglomeration behavior is reported as function of the temperature and particle morphology.

2. Computational methodology

The following describes the approaches that have been used for the two main scales involved in the formation of carbonaceous particles: the "microscale" and the "mesoscale". The microscale follows the evolution of carbon material up to particles in the nano-sized range ($\sim$thousands of carbon atoms), while the mesoscale bridges the gap from particle inception to primary particles ($\sim$millions of carbon atoms).

2.1. Microscale

The reactions involved in the formation of nanoparticles span a wide range of time scales, going from picoseconds for rearrangements that can occur on the surface of the particles to milliseconds for the formation of nanoparticles from small molecules.

Among atomistic simulation techniques, the most direct approach is molecular dynamics (MD), which follows the actual dynamical evolution of the system. However, the utility of MD is limited to processes that generally occur on a time scale of nanoseconds or less. In order to circumvent this time scale problem, we have coupled the kinetic Monte Carlo (KMC) methodology to MD in order to extend the accessible time scale by orders of magnitude relative to direct MD, while retaining full atomistic detail (Atomistic Model for particle Inception Code—AMPI) [26,27]. This methodology has provided for the first time an atomistic multiscale modeling capability for the formation of carbonaceous nanoparticles in combustion environments. More details about this methodology are reported elsewhere [27,28]. A first generation of the AMPI code has been recently developed to study the transformations that occur in combustion systems during the transition from gas phase to particle inception. Figures 1a and b show two representative structures obtained in premixed laminar flames. Particle morphology is determined by the combustion environment in terms of fuel, temperature, C/O ratio, etc. Different combustion conditions produce different gas-phase precursors and dictate the competition between bimolecular association reactions (addition or growth reactions) and
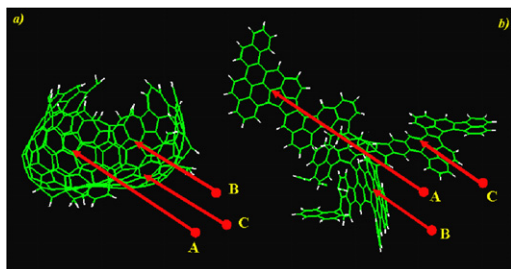
Fig. 1. Atomistic and coarse-grained representations of two carbonaceous nanoparticles (a) round and (b) flat.

rearrangement reactions which exhibit higher activation energies. Results obtained with the AMPI code have shown to agree with experimental data obtained in premixed flames. The examples reported in Fig. 1 will be used later in the paper to study the agglomeration process.

2.2. Mesoscale

Carbonaceous nanoparticle agglomeration is influenced by large length and time scale motions that extend to mesoscopic scales, i.e., 1 μm or more in length and 1 μs or more in time. In order to increase the time and length scales accessible in simulations and be able to simulate nanoparticle assembly, it is necessary to describe the particles on a more coarse-grained (CG) level. The philosophy of these CG approaches is generally the same: to achieve a simpler description of the effective interactions in a given system while not losing the ability of the resulting models to predict the properties of interest.

Typically, CG potentials of a pre-selected analytical form are parameterized either to reproduce average structural properties seen in atomistic simulations [29,30] or they are parameterized to match thermodynamic properties [31,32]. These approaches are not directly based on the underlying atomistic-scale forces. In addition, the CG approach may be further complicated due to the fact that CG potentials are expected to have less transferability compared to atomistic ones. This is because an effective interaction between the structural units intended for coarse-graining is defined by the average structure (e.g., average orientations, distances) within the complexes formed by those units in a particular phase. Poor transferability of a CG potential will undermine the reliability of simulations in which the same CG potential was used to simulate different system phases.

Recently, a force-matching (FM) method for obtaining the effective pairwise force fields for systems in condensed phases has been proposed. More algorithmic details on this method are given in Ref. [33]. Building upon this new FM methodology, a technique called "multiscale coarse-graining" (MS-CG) has been developed, which provides a systematic way for coarse-graining the interactions from the reference all-atom MD simulations. The main idea of the MS-CG method is to apply the FM procedure to the CG images from underlying atomistic trajectory/force data. The most obvious way to map an atomic group into a CG site is to associate it with its center-of-mass (CM) because the force acting on the CM of the atomic group can be straightforwardly evaluated from the atomistic MD data. The FM procedure, when applied to these data, yields the effective interaction between the CG sites as is present in the underlying all-atom simulation.

However, the coarse-graining of nanoparticle systems presents a special challenge for the MS-CG methodology because their shapes may be quite diverse, i.e., ranging from the highly symmetric C60 to more amorphous and irregular shapes. They also generally interact through the sum of many weaker interactions rather than via strong electrostatics in, e.g., an aqueous environment. However, we have recently shown that this can be accomplished with the MS-CG methodology [34].

3. Results

In this study, carbonaceous nanoparticles with two different morphologies were investigated: a particle with an aspect ratio close to unity "round" with a formula of $C_{188}H_{53}$ and a nanoparticle with a composition of $C_{202}H_{90}$ "flat", see Fig. 1. The initial configurations of the nanoparticles were obtained from the AMPI code and modified by adding missing hydrogens manually. Both round and flat nanoparticles have the size of around 17 Å in the longest dimension. The round nanoparticle consists of a network of 5–8 membered fused rings like buckyballs, whereas the flat nanoparticle has four planar aromatic moieties connected by freely rotating bonds.

Two temperatures are considered in this study to understand the influence of the temperature on the agglomeration behavior. One thousand six hundred Kelvin is a typical flame temperature, while 950 K is relative to a mesophase region where differences in structures can be observed [35].

3.1. Microscale: up to a few thousands of atoms

In order to study particle interaction at a small scale, atomistic MD simulations were carried out on two systems: the first one was composed of 32 identical round particles and the second made of 32 identical flat particles. For the interactions between nanoparticles, the CHARMM force field parameters were used. A constant NVT ensemble was used for the runs.

Interesting MD results are reported in Fig. 2 showing the importance of the nanoparticle morphologies on their clustering behavior. Two snapshots from MD simulations of a system composed of identical round particles (R, left panel) and a system of flat particles are analyzed. The simulations were performed at 950 K. 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. In addition, the clustering behavior for flat particles is quite different from the round ones: the orientation is more edge-to-edge or stacking and the interacting particles are tightly constrained.

The current models present in the literature report a simplified notion of the coagulation process, in which two particles coagulate after collision if the kinetic energy of the particles is lower than their interaction potential, which depends on van der Waals attraction and Born repulsion forces [36]. The theory yields values for the coagulation efficiency of the order of 1E-2 for nanoparticles from consideration of the interactions between particles and molecules. The results we just reported [37] using MS-CG MD simulations show that the process is much more complex that this and particle morphologies strongly influence the clustering behavior of the particle ensemble. This information is necessary to build a realistic model for soot formation.

3.2. Mesoscale: up to millions of atoms

Technically, the implementation of coarse-graining models can be divided into two distinct phases: the first is a partitioning of the system into the larger structural units to reduce the system complexity, while the second is the construction of an effective force field to describe the interactions between the CG structural units.

3.2.1. Partitioning of the system in CG sites

In order to study complex processes, such as the self-assembly or the structural transitions of nanoparticles, it is important to have a CG model with several interaction sites to account for orientational degrees of freedom of the particles. A three-site CG model was used for both configurations: the round nanoparticle was mapped into a three-site geometry by slicing it into three segments of approximately equal weight by planes perpendicular to the opening plane of the particle. The CG interaction sites were associated with the CM of the corresponding segments as shown in Fig. 1 (sites A, B and C). Similar to the round particle, the flat nanoparticle was divided into three segments in accordance to its three "wings". The CG sites were associated with the CM of the corresponding segments as shown in Fig. 1 (sites A, B and C).

3.2.2. Construction of an effective force field for CG sites

Data from the atomistic simulation described in Section 3.1 were collapsed into trajectories and forces of the CG sites, and the resulting CG
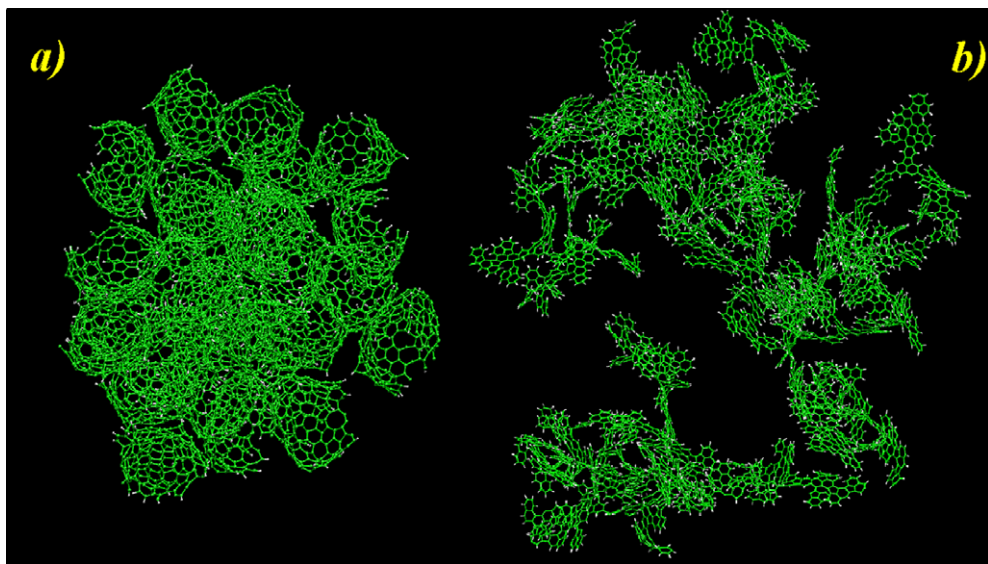

Fig. 2. Snapshots from MD simulations of two ensembles of 32 identical nanoparticles (panel (a) "round" and panel (b) "flat") at 950 K.

trajectory and force data were used as an input to the FM algorithm. The trajectory and the force data from the atomistic simulations were sampled at an interval of 0.05 ps.

The overdetermined system of linear FM equations was solved repeatedly for 12000 sets of atomic configurations from 1.2 ns of MD trajectory data, with each set consisting of two configurations and then averaged over all sets. The force field was represented by a spline over a mesh with a grid spacing of approximately 0.0025 nm. The potentials were calculated by integrating out the respective terms in the force fields and then shifting them to zero at the cutoff radius.

The classical MD simulations with the new CG models were performed using the DL POLY 2.9 computer code [38]. The tabulated force fields and potentials for all studied models are available in a DL POLY code format.

This new coarse-graining approach has been already shown to work well for carbonaceous nanoparticles and the comparison of the structural properties from the MS-CG and all-atom MD simulations is seen to be very good [34].

In order to study the formation of soot primary particles, the MS-CG MD simulations were then conducted on a system of 10,000 CG particles (or effectively 2 million atoms) for 500 ns. The density chosen for these runs is of 5E15 particles/cm^{-3}. Experimental data by D'Alessio et al. [39] report a number concentration around 1E14 for slightly sooting flames of ethylene. However, the measured value is an average and there are pockets inside the region of interest with higher density. The simulations reported here are relative to those areas since higher density will increase the collision frequency and reduce the computational time required to form the first nuclei. Figure 3 shows snapshots from the end points of these two simulations. Each particle is represented by three sites as shown in Fig. 1.

The system of round nanoparticles clearly exhibits the presence of clusters at 950 K which were observed to persist for the entire length of the simulation. The cluster size was identified around 15–20 nm. The system of flat particles shows a much lower degree of clustering for the same temperature and density. These results confirm what had been observed in more limited fashion at the microscale level and described earlier.

A further application of the MS-CG models was to study the nanoparticle aggregation behavior at higher temperatures. We therefore reparametrized the CG force fields for both the round and flat geometries using all-atom MD simulations at 1600 K. Figure 4 shows the snapshots from the MS-CG MD simulations. The system of round particles shows the presence of small agglomerates while the system of flat particles does not manifest long-lived aggregates of any kind. (Please note that the particle density in both cases is the same—the snapshots are zoomed in a different way to highlight particle aggregates.)

Figure 5 reports the resulting effective potential profiles for selected pairs of CG sites for the four simulations. In particular, the A–A site (cf. Fig. 1) interactions are represented in the figure. The minimum for the round particles is located at a distance higher than the flat ones. This is due to the particle morphology and the fact that as reported in Fig. 2, the round particles prefer to cluster with a back-to-back orientation and 1.5 nm is about the diameter of the particles. The flat ones cluster in an edge-to-edge orientation and the minimum around 0.5 nm represents the distance between the two A–A wings of the particles themselves.

For the round particles the well pronounced agglomeration noted at low temperature disappears at 1600 K where the high temperature causes an increase of the rotational energy and on average the interactions become more repulsive. The second derivative of the potential curves, evaluated at the minimum, is an indication of how much force is necessary to stretch the interparticle bond. The round system and the flat system at 950 K obviously show the strongest agglomeration. The effective potentials for flat particles present two barriers (around 0.6 nm at 1600 K and 0.8 at 950 K) indicating that the particles are more hindered in their interaction than the round ones. The fact that the effective CG site–site potential at 950 K shows two minima is indicative of more structure associated with the flat system, while the round particles pack in a disordered lattice behavior.

To get more insights on the structural agglomeration of the flat ensemble, we magnified into the system and analyzed the behavior of a smaller ensemble of 1000 flat particles at 950 K. The MS-CG MD simulation was conducted using periodic boundary conditions at constant NPT. This arrangement at constant pressure mimics the fact that we are looking more deeply into the interior of the agglomerates. Figure 6 depicts a snapshot of the nanoparticle agglomerates,
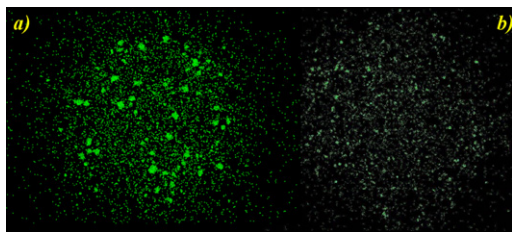

Fig. 3. Snapshots from CG MD simulations using three-site CG models of round [panel (a)] and flat [panel (b)] nanoparticles at 950 K.
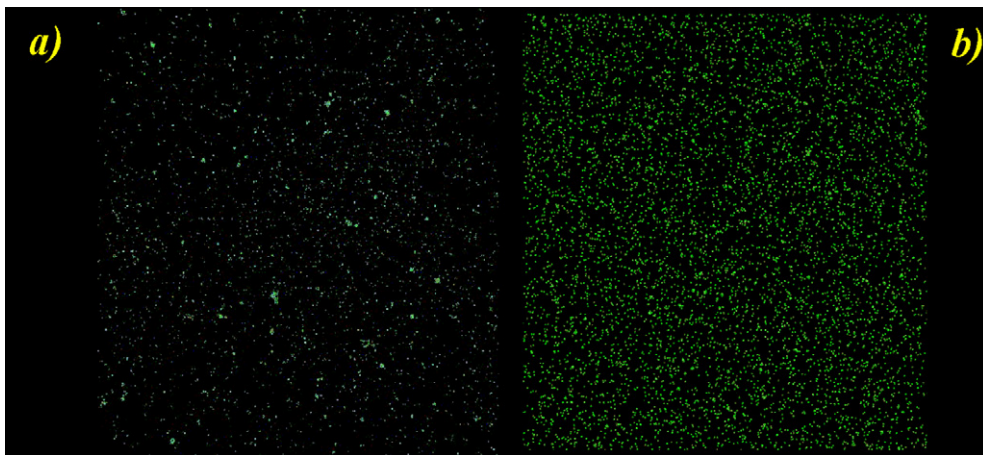
Fig. 4. Snapshots from CG MD simulations using three-site CG models of round [panel (a)] and flat [panel (b)] nanoparticles at 1600 K.
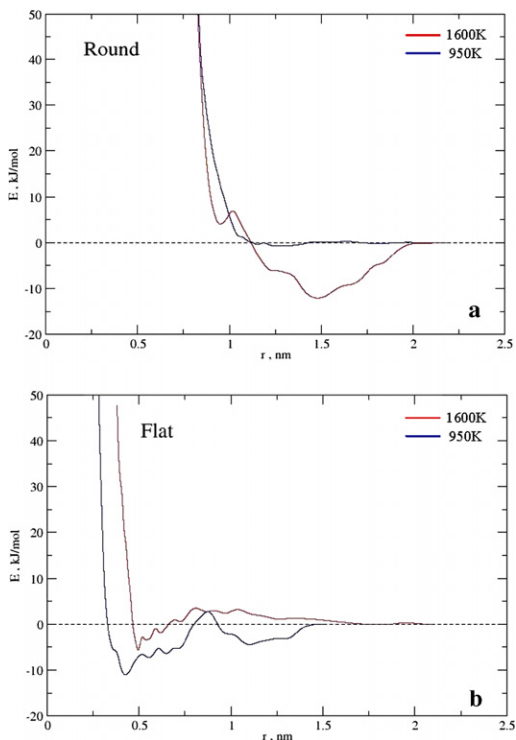

Fig. 5. Effective pairwise potentials for selected pairs of CG sites of round (a) and flat (b) nanoparticles as functions of the intersite separation calculated by the FM method.

work will be conducted on mixed systems with particles of different sizes and morphologies. Also, the results reported in this paper are relative to the early nucleation of the particles. Once the first nuclei are formed the process becomes much faster than the one reported in the figures.

At the same time, the capability of the MS-CG approach to develop the CG parameters "on the fly" from the actual atomistic-level forces coming from a full MD is very important in the study of particle formation in combustion. The newly nucleated particles grow by coagulation and coalescent collisions as well as surface growth. All these processes happen at the same time and while the MS-CG approach can describe particle coagulation, the surface growth needs to be carried out
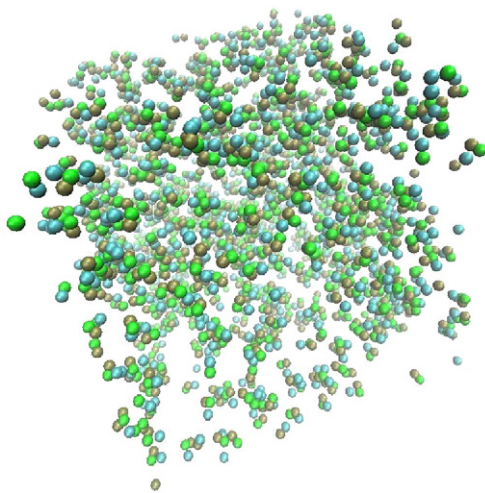
Fig. 6. Snapshot of 1000 flat particle agglomerates, showing a chain-like agglomeration behavior.

showing a chain-like agglomeration of the particle ensemble.

It is important to note that the cases analyzed here represent two extremes of the real picture and are used to analyze two conceptual limits. Future

at the atomistic level. The changes that can occur on single nanoparticles due to surface growth at the level of the atomistic MD (AMPI code) might then be propagated upward to the MS-CG effective force field via the force-matching algorithm in a multiscale fashion. This will be the topic of future methodology development.

4. Conclusions

The recently developed MS-CG method for obtaining effective pairwise CG force fields from atomistic force and trajectory data has been shown here to be very successful in developing CG models for agglomerating systems of carbonaceous nanoparticles in combustion environments. The agglomeration process occurs in several steps: the first step is represented by nucleation leading to the formation of small particles. Then, coagulation coupled with coalescence occurs: initially, coalescence dominates, producing spherical particles. As the rate of coalescence becomes lower than the coagulation rate, the aggregates of primary particles are formed. The approach presented in this paper provides a connection between the various time and length scales in the nanoparticle self-assembly problem, together with an unprecedented opportunity for the understanding of the atomistic interactions underlying nanoparticle aggregation and self-assembly. The MS-CG methodology indeed provides an ideal multiscale route for bridging the explicit atomistic representation of the nanoparticles produced by the AMPI simulation method with a more coarse-grained representation necessary to study the agglomeration of the nanoparticles into the primary soot particles, which in the end can effectively involve millions of carbon atoms. The results reported here represent the first attempt to describe the formation of large collections of primary soot particles of ∼20 nm in size, using coarse-grained MD simulations of effectively 2 million carbon atoms at flame temperature conditions for microsecond timescales, complete with chemical and structural information bridged upward from the atomistic-scale.

In the future, the MS-CG approach can be applied to nanoparticle systems containing a variety of geometries. One possible complication will be an increase in the number of CG interaction sites of different types (i.e., a larger number of species found in a CG representation of the system). However, this problem may be minimized by grouping and averaging classes of CG sites together, as well as their site–site effective interaction potentials.

The new MS-CG models of nanoparticles may also allow us to also study the phase transitions to orientational alignment of the bigger carbonaceous primary particles, which are likely responsible for the experimentally observed structures of carbonaceous clusters found in lower temperature electron micrograph images.

The knowledge of the structures of soot precursors, obtained with these atomistic methods, can supply valuable guidance to the development of soot formation models. This new approach can further provide information to the phenomenological models present in the literature on properties that can be computed only knowing the structure of the material. By understanding the chemical structures of recently formed nanoparticles and their agglomerates, mechanistic pathways can also be hypothesized to provide a linkage between current models for homogeneous gas-phase molecular growth and soot particle formation and growth [9–40].

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Comments

R.A. Dobbins, Brown University, USA. Do you see evidence of stacking of planar PAH molecules that would account for the Bragg reflections that are found in laboratory studies of dark field TEM and X-ray diffraction? These reflections are a manifestation of the carbonization process [1,2].

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Reply. This is a very good point. As today the potential we have does not include dispersion interactions and it makes difficult to describe the PAH stacking. Our next step will be to implement the potential.

●

M.C. Lin, Emory University, USA. The energies of triplet states of poly-aromatic hydrocarbons (PAHs) are known to be very low and accessible under sooting conditions. Did you include the interaction of those low-lying triplet states in your kinetic Monte Carlo/MD calculations (for example by triplet-triplet annihilations)?

Reply. This is definitely a good point and we are working on this right now.

●

Horst-Henning Grotheer, DLR Stuttgart, Germany. Is there any experimental evidence for the real existence of your beautiful particles? Have the assumed building elements, i.e., adducts of aromatic compounds containing 5 member rings and aromatic radicals, ever been detected in mass spec? Can you think of a bridge between your particle formation model and the more conventional one which includes stacking of PAHs and which has been experimentally verified through the detection of Bragg reflections?

Reply. PAH stacking is a very important step in the formation of particles. The potential we are using for the calculations does not include dispersion interactions responsible for the stacking interactions. We are in the process of implementing the potential adding this feature. This will make it possible to describe the stacking of PAH.

●

Houston Miller, George Washington University, USA. In some old work of ours [1] as well as some very recent work [2], much deeper attractive potentials have been found for non-chemically bound PAH clusters. For example, in Rapacidi et al. [2], the binding energy for (pyrene)$_2$ is nearly 55 GJ/mde and (ceronene)$_2$ is approximately 80GJ/mde. Your work found much weaker attraction. Could you comment on the possibility for condensation of your particles at flame temperature if a deeper attractive potential existed?

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Reply. This is a very good point. One of our goals is not to implement the potential we have been using and determine if a deeper potential will influence particle interactions especially at high temperatures.