Nucleation of soot nanoparticles from polycyclic aromatic hydrocarbon precursors

(Google meet: https://meet.google.com/mmp-xcab-gda)

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Introduction

Understanding of the soot formation process is crucial for reduction of harmful emissions from combustion and also for synthesis of various important carbon structures. It is widely accepted [1] that nucleation of carbon nanoparticles in flames comes via intermediate stage of formation of polycyclic aromatic hydrocarbons (PAH) and their dimerization, but still precise physical and structural properties of the nanoparticles in the early stages of formation and nucleation mechanism still remain unknown. In this work we describe nucleation kinetics of soot particles formed from large PAH structures with more than 60 atoms. Reax force field [2] is selected for MD simulations at temperature ranging from 2000 K to 2700 K. Structure of soot nanoparticles is examined by comparing parameters such as hybridization, H/C ratio, distribution of carbon fringe length and tortuosity under various thermal conditions. In addition we propose a method for partitioning the soot structure using the clustering algorithm to model the process of soot fragmentation at high temperatures. Also, mechanisms of dimers formation in PAH (e.g., coronene) at 2250 K are considered in this work.

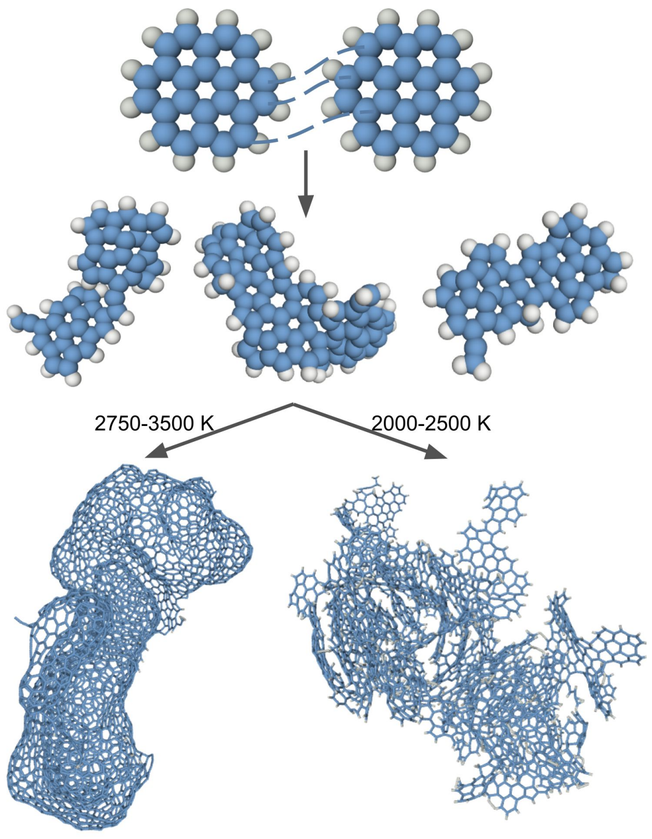

Figure 1. Carbon structures obtained in MD simulation.

Model

All MD calculations are performed using LAMMPS program package [3] with reactive interatomic potential ReaxFF. NVT ensemble is chosen for simulations. ReaxFF model [2] is a general bond-order-dependent interatomic potential which takes into account the breaking and the formation of chemical bonds. The ReaxFF potential divides the system potential energy into various contributions that depend on the bond order (except Van der Waals and Coulomb terms):

$$E_{system}=E_{bond}+E_{val}+E_{tors}+E_{vdW}+E_{Coulomb}+E_{over}+E_{under}+E_{pen}+E_{conj},$$

where E_{bond} describes the bond energy between atoms, E_{val} describes the interaction of atoms through valence angles, E_{tors} is the energy of torsion (four-particle) interactions, E_{vdW} and $E_{Coulomb}$ are the energies which represent the non-bonded interactions.

Simulation step	0.1 fs
Number of atoms	5168 Carbon: 3741 Hydrogen: 1427
Cell size	100×100×100 Å^3
Gas phase density	0.077 g/cm^3

Temperatures	2000, 2125, 2250 and 2400 K
Simulation time	8 ns

Soot nucleation from PAH precursor

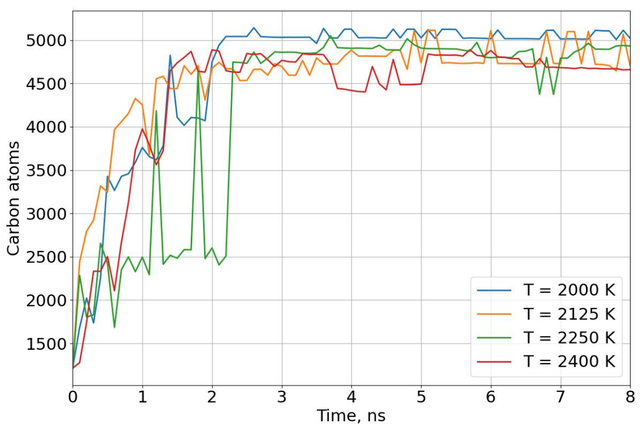

Figure 2. Size of largest carbon cluster

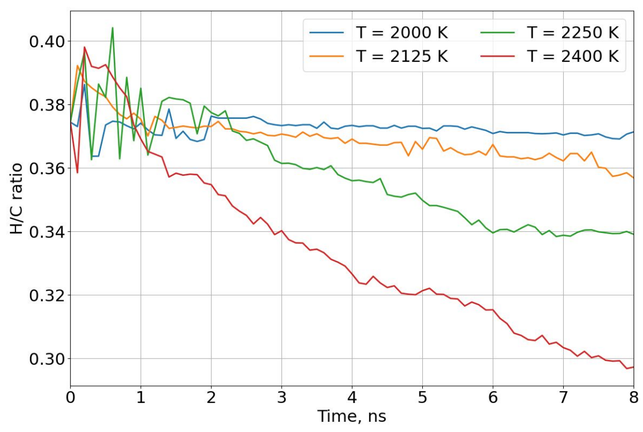

Figure 3. H/C ratio in carbon cluster

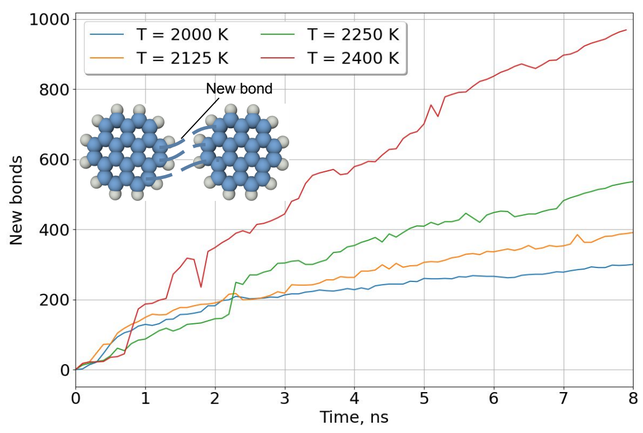

Figure 4. Number of newly formed bonds between atoms from different molecules

In Figure 1 evolution of system at 2000-3500 K is presented (blue spheres indicate carbon atoms, white spheres indicate hydrogen). It is expected that PAH molecules will collide and form large cluster. Main mechanisms of PAH clusterization is physical (without breaking and formation of chemical bonds) and chemical nucleation [5].

We calculate number of carbon atoms in largest cluster to analyse clusterization kinetics. It is assumed that atom belongs to the cluster if the distance to at least one of the particles in cluster is less than r_{cut}=1.85 Å. Figure 2 shows the dependence of size of the largest cluster on time. At 3 ns all clusters reach maximum size and when main mass growth process stops particles begin to anneal. Figure 3 shows the relation of carbon atoms to hydrogen atoms in largest particle. The rate of dehydrogenation increases drastically with temperature growth. Abstraction of hydrogen from surface of carbon particle drives process of crosslinking between different carbon fringes. To examine crosslinking process and differences in particle structure we plot the number of new bonds between atoms that belong to different molecules at the initial step. In Figure 4 one can see that the rate of crosslinking increases with temperature which results in more graphitised structure of carbon particle. At the end of simulation mass density of particles is about 1.3 g/cm^3. This result is consistent with experimental findings [7].

Conclusions

- Constant temperature molecular dynamics simulations were performed on the nanosecond timescale to investigate the influence of the formation temperature on the structure of incipient carbon soot nanoparticle. We observe that at higher temperatures covalent bond rebuilding during clusterization is more intense which results in more covalently interconnected and therefore more stable structures.
- The process of high temperature decomposition was modeled with usage of divisive clustering algorithm. The number of bond splits needed to complete soot particle decomposition grows with temperature. The properties of subclusters in particle such as tortuosity and fringe length were examined.

References

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Modeling of thermal decomposition

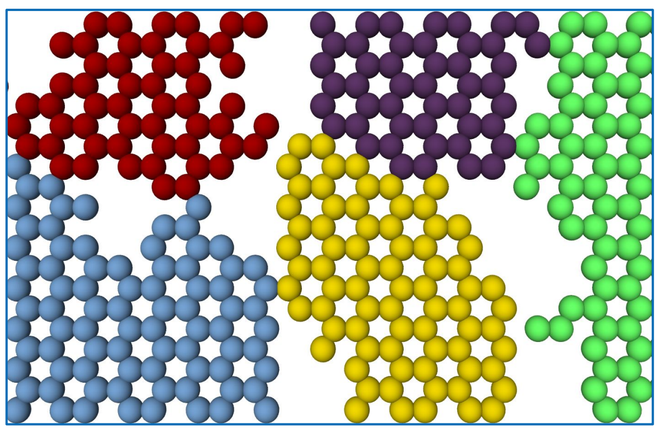

Figure 5. Example of algorithm work for perforated graphene sheet

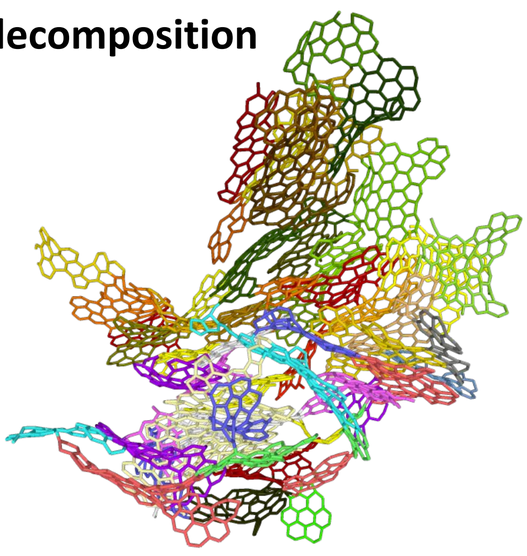

Figure 6. Splitting of soot particle formed in MD-simulation at 2250 K into subclusters (fringes)

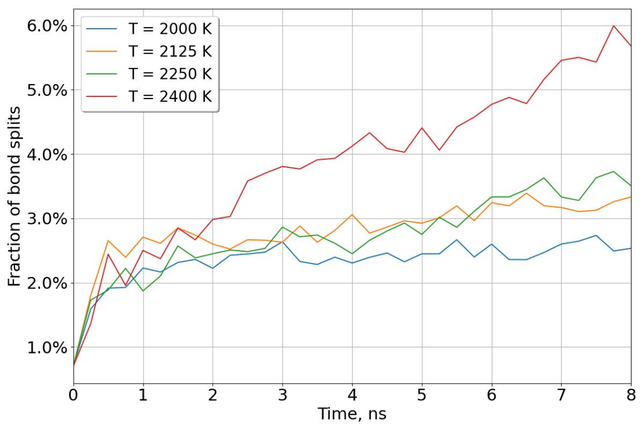

Figure 7. Number of splits needed to complete structure decomposition

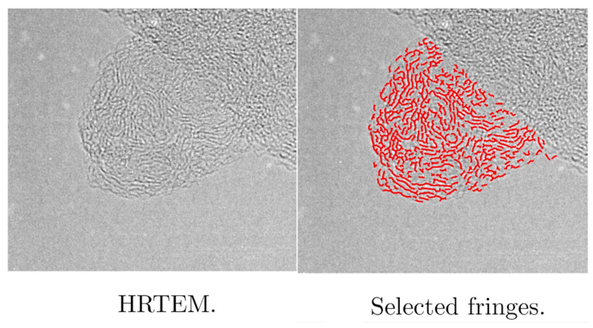

Figure 8. Example of HRTEM images with observed carbon fringe structure [6]

In the experiment soot particles are heated with laser impulses until they fall apart into pieces about 1 nm, the critical resolution of particle detection[8]. In order to study the process of high temperature decomposition of soot particles we use divisive clustering algorithm [4]. The purpose was to split the particle into pieces, containing less than 100 carbon atoms (which corresponds to the 1 nm experiment resolution), providing minimum cut. Figure 5 shows algorithm work for simple case of perforated graphene sheet. Figure 6 demonstrates the result of splitting procedure for the soot particle formed at 2250 K. Figure 7 shows the number of splits needed for the complete decomposition of soot structure into carbon nanoflakes with the given number of atoms. The number is greater with higher temperature and grows with particle residence time which corresponds to the process of crosslinking shown in Figure 4.

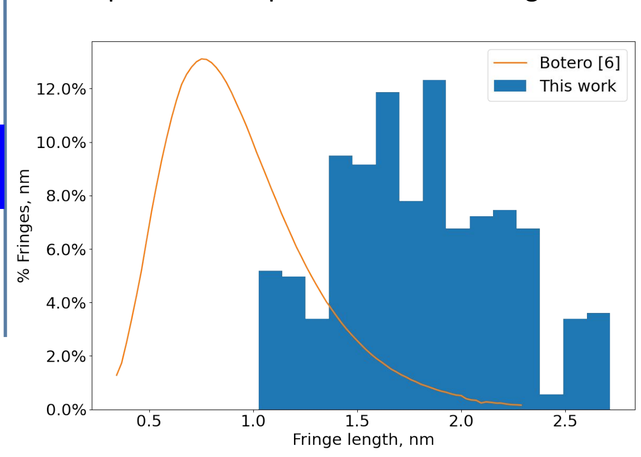

Figure 9. Distribution of fringe length

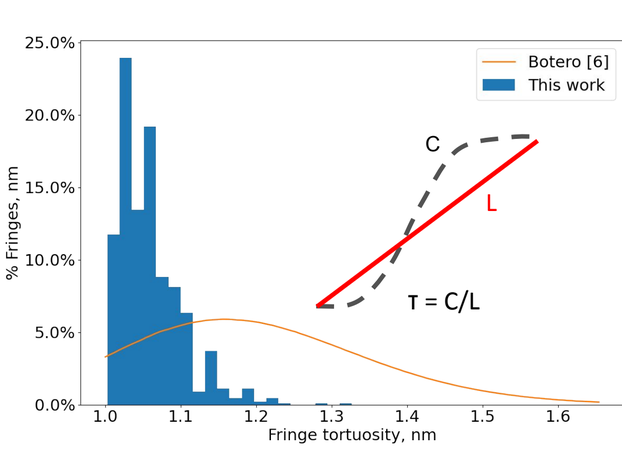

Figure 10. Distribution of fringe tortuosity (τ)

After the splitting of carbon particle into carbon fringes we compare their structural properties (i.e. distribution of fringe length and tortuosity) with the same properties obtained from the HRTEM images [6]. The comparison of experimental distribution with obtained in our work (Figures 9,10) shows that applied clustering algorithm provides a good result consistent with experimental, especially considering the fact that the form of the distributions may vary with different flame conditions.