Kinetics of carbon soot growth from PAH precursors: atomistic modeling

Klim Goldshtein[1,2], *Nikita Orekhov*[1,2]
[1] Joint Institute for High Temperatures (JIHT RAS)
[2] Moscow Institute of Physics and Technology
https://meet.google.com/jgq-rwvc-coz

Introduction

Soot formation is an important process which affects fuel combustion and synthesis of carbon structures. The formation and growth of soot structures are dependent on the conditions of the process, but the exact mechanism has not been understanded well [1, 2]. Using molecular dynamics methods, we focus on the dependence of soot structures growth on temperature in 2250 K to 3000 K temperature range. This way, we studying collisions between soot structures obtained from PAH (polycyclic aromatic hydrocarbons) and PAH itself. The reasoning is to find the dependence between soot-PAH complex and morphology of the soot structure. The study provides better understanding of the kinetics of soot structures grow, which is the main objective of our research. The results were obtained using LAMMPS with ReaxFF [2] potential.

Model

Given the problem above, we prepared two different soot structures formed in 2250 K (so-called intermediate particle, corresponds to the intermediate polyaromatic structures in the real combustion reaction, fig.1) and 3000 K (so-called round particle, corresponds to the finally formed soot structures, fig.2) temperatures. Using the MD methods we calculated the trajectories of possible collisions between nanoparticle and surrounding coronene molecules. Collisions between soot nuclei and surrounding molecules are common in combustion, and are quite important for particle formation [4]. The simulation time of one collision is about 15 ps.

Collision energies analysis

Energy profiles of the collisions were plotted (fig. 3, fig. 4), giving some insights on the difference between collisions with different structures. They were also compared with the energy of collision of PAH with graphene sheet, which has much more simple morphology. Thus, energies of the PAH collisions with soot structures is proved to be smaller than ones for graphene sheet. It is also found out that collisions with round particle also gives the bigger energy profile, which can indicate that round particle has better morphology for PAH attachment

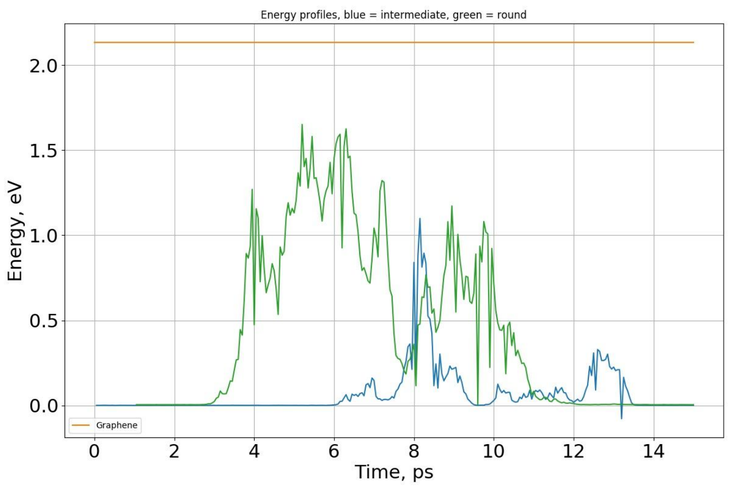

Fig.3 Profiles of energies at T = 2250 K
Blue - intermediate particle, green - round

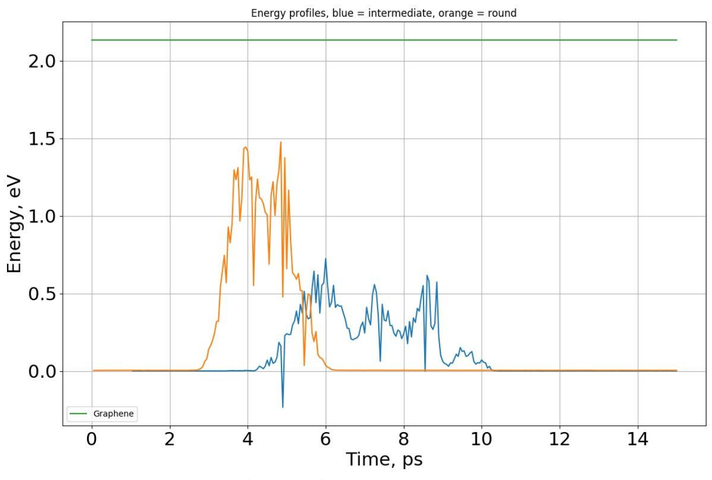

Fig.3 Profiles of energies at T = 3000 K
Blue - intermediate particle, orange - round

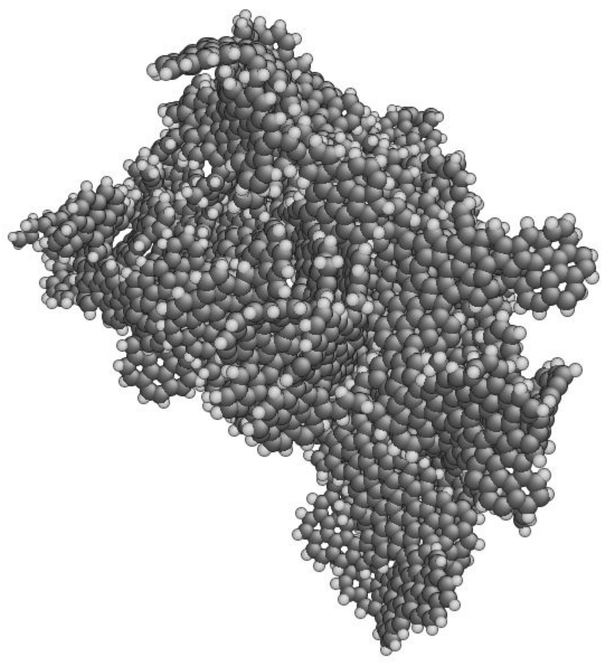

Fig.1 Intermediate soot nanoparticle

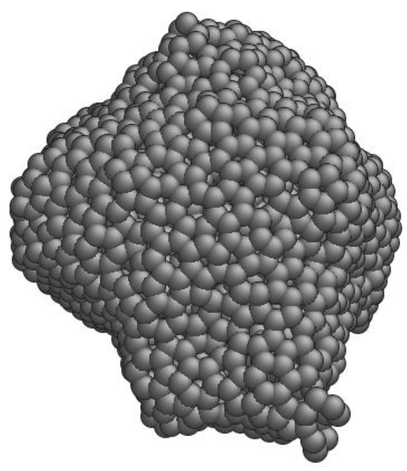

Fig.2 Round soot nanoparticle

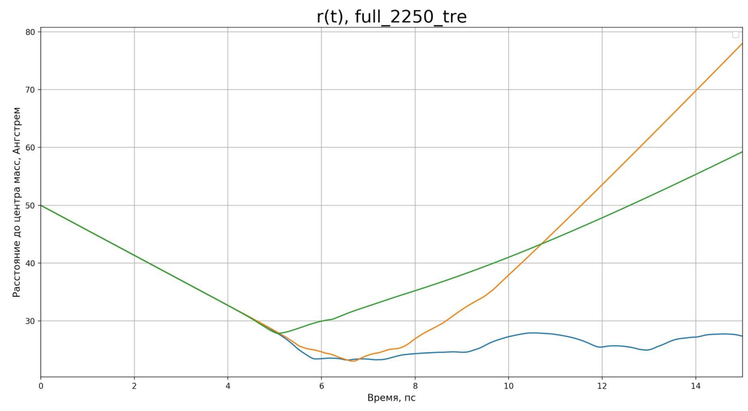

Fig.5 Sample trajectories for 3 types of collisions

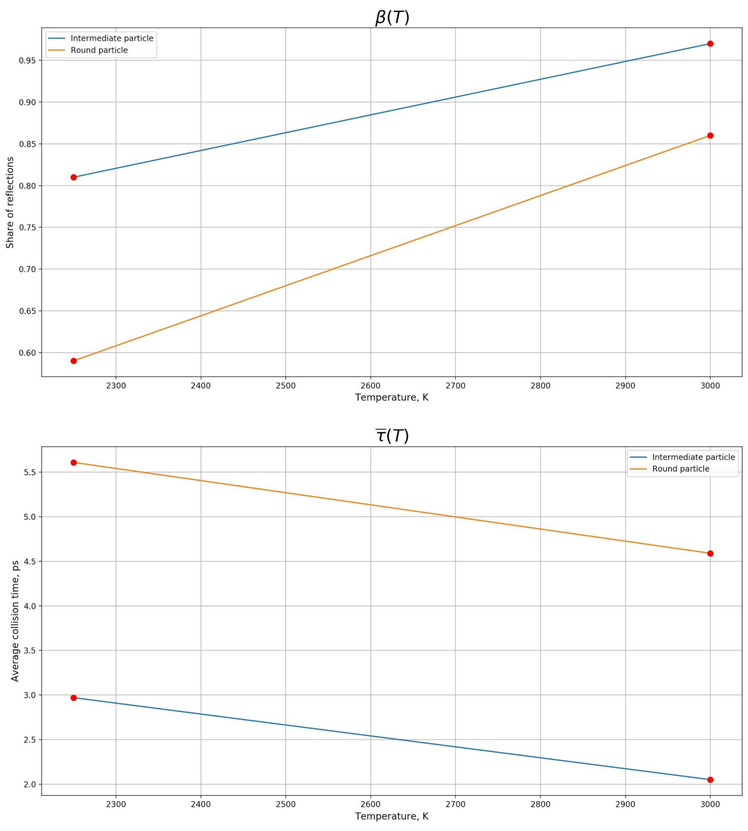

Fig.6 Rate of effective collisions (top)
Average time of collision (bottom)

Methods

All MD calculations are performed using LAMMPS program package with reactive interatomic potential ReaxFF. The simulations are based on the interaction of a coronene molecule and prepared soot structure (N atoms for intermediate one and M atoms for round one) at two different temperatures. Simulations were made using NVE ensemble. ReaxFF model 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.

$$E_{\text{system}} = E_{\text{bond}} + E_{\text{over}} + E_{\text{angle}} + E_{\text{tors}} + E_{\text{vdWaals}} + E_{\text{Coulomb}} + E_{\text{Specific}}.$$

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

Trajectories & Statistics

Trajectories of the PAH were also studied to find out what is the probability of attachment of PAH and how residence time during the collision is distributed. Conditionally, the cases can be referred as immediate reflection (green on fig. 5), reflection after residence (orange), and attachment (blue). Thus, we can plot the dependence of the average residence time and share of reflections (fig. 6). It can be seen that for both round and intermediate particle share of reflections grows as the temperature increases, while the average residence time is decreasing.
One more thing to analyze is the distribution of residence time during the collision. The histograms for the N = 100 cases of collision is shown on the fig. 7. It can be seen that histograms for round particle have larger tail.

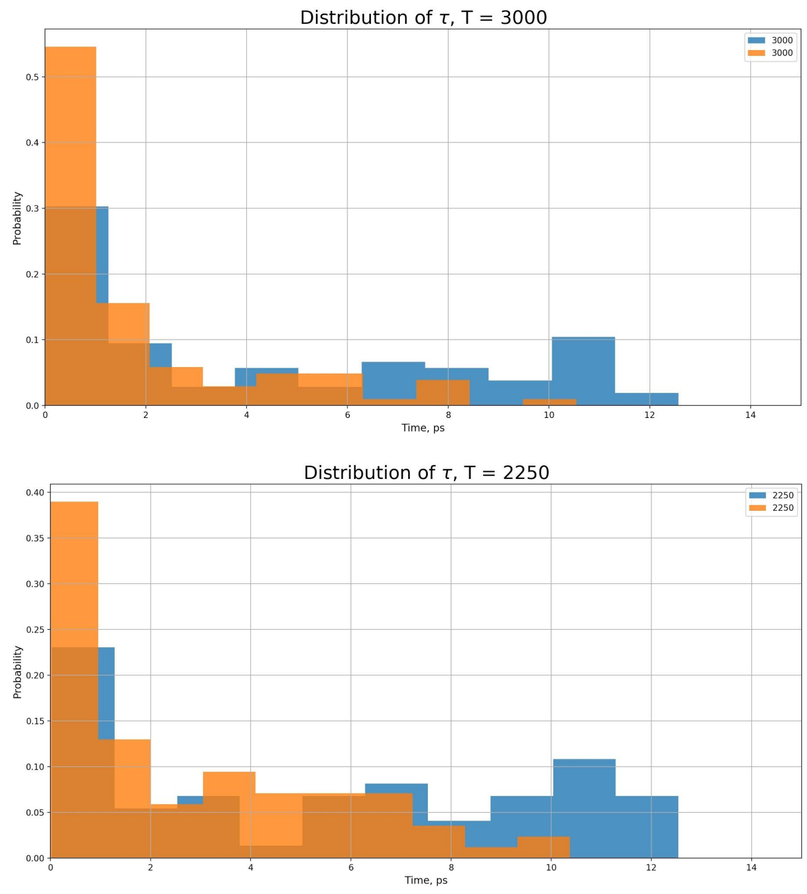

Fig.7 Histograms of residence time
Blue - round particle, orange - intermediate

Conclusion

Molecular dynamics simulations were performed on the picosecond timescale at two temperatures to investigate the influence of the soot morphology on the efficiency of carbon nanoparticle growth. We observe that it is a significant factor, affecting the efficiency of the soot growth a lot. It can also be seen that intermediate particles are less likely to append gaseous PAH molecules than round ones. The difference in collisions energy profiles between two types of structures is also significant.

Links

[1] Johansson K O, Head-Gordon M P, Schrader P E, Wilson K R and Michelsen H A 2018 Science 361 997–1000
[2] Mao Q, van Duin C T and Luo K H 2017 Carbon 121 380–388
[3] E. V. Gurentsov, A. V. Eremin, and E. Y. Mikheyeva, High Temperature 55, 723–730 (2017)
[4] Mao Q, van Duin C T and Luo K H Phys. Chem. Chem. Phys. 2019, 21, 3849-3856