Nucleation and structure of soot particles: Investigating the role of curved aromatics and ions

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Summary

A complete description of carbonaceous particulate behaviour in combustion processes requires detailed knowledge of the gas-to-solid transition of hydrocarbon molecules to form soot particles. This process is poorly understood due to low species concentrations, short time frame, and small length scales, which limit experimental measurements. Molecular modelling tools are not restricted by these conditions and therefore provide valuable insight into the behaviour of soot nanoparticles. It is known that curved polycyclic aromatic hydrocarbons (cPAHs) possess significant dipole moments and are found within flames[1]. Recent work suggests that long-range interactions between these curved species and chemi-ions may be important to the soot formation mechanism[2]. This work explores the impact of ion-cPAH interactions in stabilising nascent soot particles and works towards the development of a heterogeneous nucleation model for these species. Molecular dynamics simulations provide information on homogeneous and ion-induced heterogeneous nucleation of cPAHs. The formation dynamics and internal particle structures are explored across a range of temperatures. These results provide insight into how the interactions between cPAHs and ions affect the formation and structure of soot nanoparticles and provide valuable information towards expanding current soot models.

Introduction

Carbonaceous particles, known as soot, are by-products of incomplete combustion that negatively impact combustion devices, human health and the environment. There is a strong desire to mitigate these undesired effects through the use of clean fuels or redesign of combustion devices. This requires detailed knowledge of the complex physical processes involved in the formation and growth of soot particles. The interactions between curved polycyclic aromatic hydrocarbon molecules (cPAHs) and ions are believed to play a significant role in soot formation[2]. Recently, we have developed an intermolecular potential, curPAHIP, that is able to capture the properties and interactions of cPAHs and have explored the ion-induced nucleation behaviour of the smallest cPAH corannulene[3]. The aim of this work is to explore the significance of cPAH and ion interactions in a flame environment and the resulting particle properties and structures.

Methods

This work uses advanced molecular dynamics simulations to explore the nucleation and particle growth of soot-representative cPAHs as well as their energy-dependent nanostructures. The interactions between cPAHs are described using the new curPAHIP potential, which is able to capture the polarity and enhanced interactions of cPAHs[3]. Several cPAH sizes and ratios are investigated, along with systems containing planar PAHs and ions, to explore the homogeneous and heterogeneous particle structures and properties.

Results and discussion

Nucleated clusters provide insight into whether cPAH-ion interactions are significant enough to form stable particles at flame temperatures, and suggest nucleation rates and nuclei sizes. It was seen that heterogeneity has a significant effect on particle nucleation, with electrostatic interactions between polar components dominating. The size and ratio of constituent cPAHs have significant effects on the internal structure and surface properties of nanoparticles. Homogeneous cPAH particles are found to be tightly packed and less stacked than their planar PAH counterparts. The constituent cPAH size plays a role in the molecular arrangement, with large 15 ring cPAHs ($C_{42}H_{14}$) displaying long-range order absent in nanoparticles containing small 7 ring cPAHs ($C_{20}H_{10}$). Binary particles containing cPAHs of different sizes, such as those shown in Figure 1, display a core-shell structure in which the larger molecules make up the core and the smaller molecules comprise the shell, as seen with planar PAH nanoparticles. This trend is not strongly influenced by the molecule ratio. In addition, the presence of planar PAHs and ions within cPAH nanoparticles promotes arrangements likely to be indicative of mixed systems. These results provide information on the self-assembly of curved carbons, as well as insight into the energetic and structural properties of the resulting nanoparticles, useful for an accurate understanding of the dynamic nature of these systems.

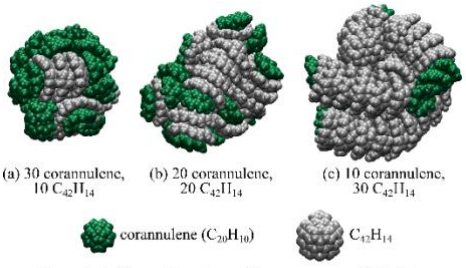

Figure 1: Stable configurations of heterogeneous cPAH clusters containing 40 molecules of corannulene and $C_{42}H_{14}$ molecules in different molecular ratios. Smaller corannulene molecules are coloured green and larger $C_{42}H_{14}$ molecules are coloured grey.

Conclusions

This work uses advanced molecular dynamics simulations to explore the nucleation behaviour and properties of nanoparticles containing curved aromatics. Large timescales and temperature ranges were sampled to provide insight into the dynamic behaviour of curved aromatics in homogeneous systems as well as those containing planar molecules and cations. These results provide valuable information for soot formation and growth and can be used to expand current soot models.

References

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