Soot particle structure: Insights from molecular dynamics and Monte Carlo simulations

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Incomplete combustion produces carbonaceous particulate matter, known as soot, which negatively affects combustion devices, human health and the environment. The development of soot prediction models and mitigation strategies requires an accurate knowledge of soot particle formation and structure. Electron microscopy has revealed that mature soot particles often have a core-shell structure, in which the molecules near the centre of the particle differ in size from those in the surface layers [1]. However, it is unknown what interactions cause this partitioning and to what extent it is present in nascent particles.

In this work, the behaviour of heterogeneous polycyclic aromatic hydrocarbon (PAH) clusters was investigated using two independent molecular modelling methods to understand the structure of nascent soot particles. Clusters of up to 100 molecules containing combinations of the different sized PAHs circumcoronene, coronene, ovalene, or pyrene were evaluated. Replica exchange molecular dynamics (REMD) simulations sampled many configurations at high and low temperatures to determine stable low energy structures [2]. These results were compared with a novel Sphere Encapsulated Monte Carlo (SEMC) method, developed here to extend basin-hopping minimisation methods for use with aromatic molecules.

Both the REMD and SEMC simulations showed that the most stable cluster structures consist of parallel columns of stacked PAHs in a core-shell structure, in which the larger PAHs are located in the core, and the smaller PAHs are found in a surrounding shell, as seen in Figure 1. This is an inverse partitioning compared to that seen in mature soot particles, proposing a unique structure for nascent soot particles and suggesting that the molecular organisation determined by intermolecular interactions is not responsible for the core-shell structure of mature soot. These results present the first simulations of soot-sized heterogeneous PAH clusters and can help further understanding of soot formation and growth processes.

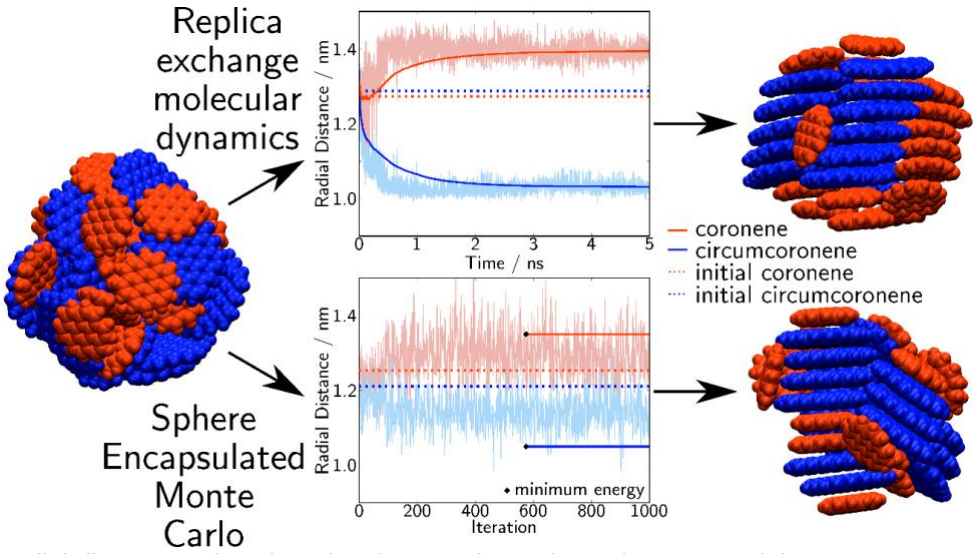

Figure 1: Radial distances of each molecule type shown for a cluster containing 16 coronene molecules (coloured red) and 16 circumcoronene molecules (coloured blue) using replica exchange molecular dynamics simulations and the Sphere Encapsulated Monte Carlo method. Initial and final cluster snapshots are also shown.

[1] T. Ishiguro, Y. Takatori, and K. Akihama. *Combust. Flame,* (1997), **108**, 231–234.
[2] K. Bowal, J.W. Martin, M. Kraft. *Carbon*, (2019), **143,** 247-256.