

5F07: THERMODYNAMIC OF POLY-AROMATIC-HYDROCARBON CLUSTERING AND THE EFFECTS OF SUBSTITUTED ALIPHATIC CHAINS

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In the last few decades the understanding of the processes related to the formation of soot has progressed considerably. However, the mechanisms that are responsible for the nucleation of soot are still unclear. While there is a consensus that the formation of soot nuclei is related to two classes of mechanisms (physical and chemical growth), their relative importance is still debated. In particular, the aggregation of polycyclic aromatic hydrocarbons (PAHs), especially pyrene, has been proposed as the key step for soot formation, but strong experimental or computational proofs are still missing. To shed light on this issue, in this work we report on the free energy (FE) profiles of the dimerization and trimerization process of several PAHs, using molecular dynamics simulations together with the well-tempered Metadynamics algorithm. With this approach, we are able to efficiently sample all the important space configurations without making any assumptions, except for the interatomic potentials that govern the dynamics of the atoms. The results of these simulations show that already at 1000 K only the formation of dimers of species such as ovalene or bigger are favored over their corresponding free monomers, ruling out the simple stacking of pyrene as the main step for soot formation. The shapes of the free energy profiles also illustrates that there are no barriers in the exploration of the phase space and therefore that the dimerization process itself is not kinetically controlled. Moreover, factors like the symmetry of the monomers and the presence of aliphatic chains attached to the PAHs appear to play a key role for a correct description of the physical agglomeration leading to soot nuclei.

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